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(54) Process for the protection of stone materials, marble, bricks and concrete from decay caused by atmospheric agents and pollutants or by mural writings with paints, inks and the like.

(57) The present invention relates to a process for the protection of stone materials, marble, bricks and concrete, and of structures made from such materials, from the decay caused by atmospheric agents and pollutants or by mural writings with paints, inks and the like. The process comprises applying to the surface of said materials or structures a mixture which comprises:

1) polytetrafluoroethylene in the form of a fine powder;
2) a perfluoropolyether not bearing functional groups and/or

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3) a perfluoropolyether or a fluoropolyether having one chain end, or both chain ends, constituted by functional groups which are capable of forming a chemical and/or physical bond with the material to be protected.

PROCESS FOR THE PROTECTION OF STONE MATERIALS, MARBLE, BRICKS AND CONCRETE FROM DECAY CAUSED BY ATMOSPHERIC AGENTS AND POLLUTANTS OR BY MURAL WRITINGS WITH PAINTS, INKS AND THE LIKE

The present invention is concerned with a process for the protection of stone materials, marble, bricks and concrete, and of structures made from such materials, from decay caused by atmospheric agents and pollutants or by mural writings with paints, inks and the like.

It is known that the decay of building materials, such as marble, stone, bricks, and concrete, and of structures built from such materials, is caused by chemical and physical phenomena, both of which take place in the presence of water.

A physical phenomenon which acts on all building materials is that due to the succession of frost and thaw, which causes water absorbed inside the pores of the same material to freeze and the corresponding ice to melt, with changes in specific volume, and stresses which cause fractures, or separation of individual particles which constitute the material.

Another chemical-physical phenomenon is the process of dissolution in water of limestone which is present in marble as an essential component, and in stone as a binder, consequently having no cohesion between the granules.

Even more important in the decay of materials and structures exposed to outdoor environment is the set of phenomena of chemical nature: these are essentially constituted by the attack on carbonate portions of the material or of the structure, by agents and polluting substances contained in atmospheric air (carbon dioxide, sulphur dioxide, nitrogen oxides, hydrogen chloride, hydrogen sulphide); such pollutants react with the material in the presence of water, their concentration being particularly high in rain.

It is well known that, in order to eliminate or at least reduce the above-mentioned drawbacks, the speed of penetration of the water from the external environment into the interior of the material to be protected must be considerably reduced.

In order to achieve this purpose, chemical compounds exerting a water-repellant action are applied usually to the outer surface to be protected.

US-A-4499146 discloses the use for such a purpose of neutral perfluoropolyethers, i.e. perfluoropolyethers not provided with functional groups. EP-A-192493 and 215492 disclose the use of perfluoropolyethers wherein either one chain end, or both chain ends, are consituted by functional groups, such as amide groups or ester groups. The same European patent applications also disclose the use of functionalized perfluoropolyethers in mixture with neutral perfluoropolyethers.

The use of these perfluoropolyethers, either functionalized or not, gives good results in the protection of marble and of stones with low and medium porosity. Not so good results are obtained with high-porosity materials, i.e., with materials having 20-40%, or more, of porosity.

An object of the present invention is to provide a process which supplies an excellent protection both to low- or medium-porosity materials, and to high-porosity materials.

Another object is to provide a process which provides a better protection, the amount of protecting agents relative to both functionalized and non-functionalized perfluoropolyethers, being the same.

These and other purposes are achieved by the process of the present invention for the protection of stone materials, marble, bricks and concrete, and of structures built with such materials, from the atmospheric agents and pollutants, by means of the application of protective agents on the surface of said materials and structures. This process is characterized in that the protective agents are constituted by a mixture of:

1) polytetrafluoroethylene, or a tetrafluoroethylene copolymer containing up to 12 mol % of other perfluorinated monomers, said homopolymer or copolymer being used in the form of a fine powder;

2) a perfluoropolyether not bearing functional groups; and/or

3) a perfluoropolyether or a fluoropolyether having one chain end, or both chain ends constituted by a functional group capable of forming a chemical and/or physical bond with the material to be protected, or a product of polycondensation or ethylenic polymerization of the above-said functionalized perfluoropolyether or fluoropolyether.

As tetrafluoroethylene copolymers suitable for use in the present invention, for example, those may be cited, which contain up to 10 mol % of hexafluoropropene and up to 5 mol % of perfluoroalkylperfluorovinyl-ethers, in particular perfluoropropyl-perfluorovinyl-ether, used up to an amount of 3 mol %.

The average molecular weight of tetrafluoroethylene homopolymers or copolymers is generally within the range of from 100 000 to 2 000 000.

The average size of the primary homopolymer or copolymer particles is generally comprised within the

range of from 0.05 to 0.5 μm.

The average molecular weight of the perfluoropolyether not containing functional groups is commonly comprised within the range of from 3 000 to 16 000 whereas that of the functionalized perfluoropolyethers or fluoropolyethers is commonly comprised within the range of from 500 to 20 000.

The perfluoropolyethers not bearing functional groups and functionalized perfluoropolyethers may have oxaperfluoroalkylene units belonging to the following types:

I) $(CF_2\text{-}CF_2O)$ and (CF_2O), such units being randomly distributed throughout the perfluoropolyether chain; or

II) $(CF_2\text{-}CFO)$ and $(CFXO)$, with CF_3 as the side group on the $(CF_2\text{-}CFO)$ unit,

wherein X is either F or CF_3, said units being randomly distributed along the chain; or

III) $(CF_2\text{-}CF_2O)$, $(CF_2\text{-}CFO)$ and $(CFXO)$, with CF_3 as the side group on the $(CF_2\text{-}CFO)$ unit,

wherein X is either F or CF_3, such units being randomly distributed along the chain; or

IV) $(CF\text{-}CF_2O)$; or, with CF_3 as the side group,

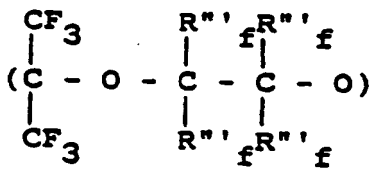
V) $(CF_2\text{-}CF_2\text{-}CF_2O)$; or

VI) $(CF_2\text{-}CFO)_{a'}\text{-}CF_2\text{-}(R''_f)_{n'}\text{-}CF_2O(\text{-}CF\text{-}CF_2\text{-}O)_{b''}$, with CF_3 as the side group,

wherein R''_f is a fluoroalkylene group, preferably containing 1 to 8 carbon atoms; n' is either 0 or 1; a' and b' are integers, and the $(a' + b')$ sum is equal to or higher than 2; or

VII) $(CF_2\text{-}CF_2O)$; or

VIII)



wherein R''_f either equal to or different from each other, is fluorine or a perfluoroalkyl group; or

IX) $(CF_2O\text{-}CF_2\text{-}CF_2O)$.

The functionalized fluoropolyethers may have the following units:

X) $(CH_2\text{-}CF_2\text{-}CF_2O)$; or

XI) $(CF_2\text{-}CF_2\text{-}CH_2O)_{p'}\text{-}R^{iv}_f\text{-}O\text{-}(CH_2\text{-}CF_2\text{-}CF_2O)_{q'}$

wherein R^{iv}_f is a fluoroalkylene group preferably containing 1 to 8 carbon atoms and p' and q' are zero, or integers and the $(p' + q')$ sum is equal to or larger than 2.

Examples of functional groups of functionalized perfluoropolyethers and fluoropolyethers are disclosed in detail as per follows.

Neutral perfluoropolyethers (i.e. perfluoropolyethers not bearing functional groups) and functionalized

per fluoropolyethers and fluoropolyethers suitable to be used in the mixture of protective agents of the present invention, are e.g. disclosed in above-cited US-A-4499146, and EP-A-192493 and 215492. For a description of these and other suitable neutral perfluoropolyethers and functionalized perfluoropolyethers and fluoropolyethers, and of their manufacturing process, reference is also made to US patents Nos. 3242218, 3655041, 3715378, 3810874, 3847978 and 4523039; to IT-A-903446; to EP-A-148492, 151877 and 224201 and to WO 87/00538 and WO 87/02992.

Neutral perfluoropolyethers of the following classes may for example be used:

$$A)\ R_f\text{-}O\text{-}(C_3F_6O)_a\left(\begin{matrix}CF\text{-}O\\ |\\ CF_3\end{matrix}\right)_b(CF_2O)_c\text{-}R'_f$$

wherein:

R_f and R'_f, either equal to or different from each other, are selected from CF_3, C_2F_5 and C_3F_7; the C_3F_6O (oxytrifluoromethyl-trifluoroethylene),

$$\begin{matrix}CF\text{-}O\\ |\\ CF_3\end{matrix}$$

and CF_2O units being randomly distributed along the chain;

a is an integer;

b and c are integers or zero;

when the (b + c) sum is different from zero, the a/(b + c) ratio is comprised within the range of from 5 to 40.

The average molecular weight is comprised within the range of from 4 000 to 10 000.

B) $CF_3O\text{-}(C_2F_4O)_d(CF_2O)_e\text{-}CF_3$ wherein the C_2F_4O and CF_2O units are randomly distributed along the chain;

d and e are integers;

the d/e ratio is comprised within the range of from 0.3 to 5.

The average molecular weight is comprised within the range of from 3,000 to 16,000.

C) $CF_3O\text{-}(C_3F_6O)_f(C_2F_4O)_g(CFXO)_h\text{-}CF_3$

wherein the C_3F_6O, C_2F_4O and CFXO units are randomly distributed along the chain;

f, g and h are integers;

the f/(g + h) ratio is comprised within the range of from 1 to 50;

the g/h ratio is comprised within the range of from 1 to 10;

X is either F or CF_3;

the average molecular weight is comprised within the range of from 4 000 to 12 000.

D) $R^3_fO\text{-}(CF_2CF_2CF_2O)_jR^4_f$

wherein R^3_f and R^4_f, either equal to, or different from each other, are $-CF_3$ or $-C_2F_5$ and

j is an integer having such a value, that the average molecular weight is comprised within the range of from 4 000 to 16 000.

As the functionalized perfluoropolyethers, for example those belonging to the following classes are used:

$$E)\ R_f\text{-}O\text{-}(C_3F_6O)_a\left(\begin{matrix}CF\text{-}O\\ |\\ CF_3\end{matrix}\right)_b(CF_2O)_c\text{-}D$$

wherein:

R_f is a perfluoroalkyl group containing from 1 to 3 carbon atoms; the C_3F_6O,

$$\begin{array}{l} CF\text{-}O \\ | \\ CF_3 \end{array}$$

and CF_2O units are randomly distributed along the chain;
a is an integer;
b and c are integers or zero;
when the (b + c) sum is different from zero, the a/(b + c) ratio is comprised within the range of from 5 to 40.
D is a -CFX-COZ′ group, wherein X is F or CF_3 and Z′ is OH, OR^5 or NR^6R^7, wherein R^5 is an alkyl group containing from 1 to 8 carbon atoms, an aromatic group or an alkylaromatic group, such as, e.g., the benzyl radical; the aromatic group preferably contains either 6 or 10 carbon atoms, and the alkylaromatic group contains from 7 to 11 carbon atoms; the aromatic group may be substituted with alkyl groups (preferably containing from 1 to 3 carbon atoms) or polyethoxy groups (preferably containing from 1 to 6 ethoxy units);
R^6 and R^7, either equal to or different from each other, can be an alkyl group containing from 1 to 8 carbon atoms or a phenyl group substituted with alkyl groups or polyethoxy groups. The alkyl groups preferably contain from 1 to 3 carbon atoms. The polyethoxy groups preferably contain from 1 to 6 ethoxy units.
The average molecular weight is comprised within the range of from 500 to 10 000.

F) $D'\text{-}(C_2F_4O)_d(CF_2O)_e\text{-}D'$
wherein the C_2F_4O and CF_2O units are randomly distributed along the chain;
d and e are integers; the ratio of d/e is comprised within the range of from 0.3 to 5;
D′ = CF_2-COZ′, wherein Z′ has the above disclosed meaning;
the average molecular weight is comprised within the range of from 1 000 to 20 000.

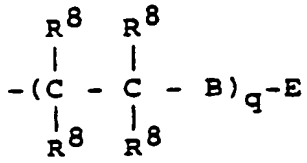
$$G)\quad R_f\text{-}O\text{-}(C_3F_6O)_a\begin{array}{l}(CF\text{-}O)_b \\ | \\ CF_3\end{array}(CF_2O)_c\text{-}CFX\text{-}YZ_p$$

wherein:
R_f is a perfluoroalkyl group containing from 1 to 3 carbon atoms; the C_3F_6O,

$$\begin{array}{l} CF\text{-}O \\ | \\ CF_3 \end{array}$$

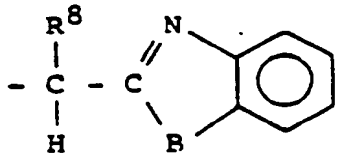
and CF_2O units are randomly distributed along the chain;
a is an integer;
b and c are integers or zero;
when the (b + c) sum is different from zero, the a/(b + c) ratio is comprised within the range of from 5 to 40.
p can be 1 or 2;
Y is a bivalent or trivalent bridging organic radical.
The average molecular weight is comprised within the range of from 500 to 10 000.
Z is a functional group capable of forming a chemical and/or physical bond with the material to be protected, and is selected from
Z1: a non-aromatic, non-fluorinated organic radical not containing active hydrogen atoms, containing two or more heteroatoms, either equal to, or different from each other and selected from O, N, S, Se and P, which are donors of electronic doublets and are located in 1-3, 1-4 or 1-5 position relatively to one another, or an aromatic radical optionally containing heteroatoms, selected from those indicated above, capable of forming coordination or charge-transfer bonds. These radicals are described in EP-A-165649 and 165650.

An example of a suitable non-aromatic organic radical is:



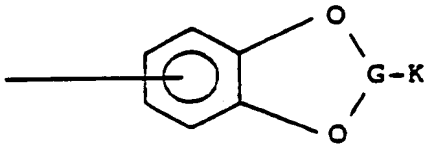
wherein R^8 is either H or an alkyl containing from 1 to 3 carbon atoms, E is an alkyl containing from I to 3 carbon atoms, B is either O or S, and q is 2 or 3.

An example of a suitable aromatic radical is:



wherein R^8 and B have the above indicated meaning.

Another example of a suitable aromatic radical is:



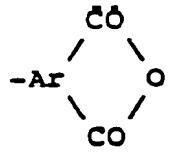
wherein G is >CH- or >CH-CH_2- and K is a hydrogen atom or an alkyl radical containing from 1 to 3 carbon atoms.

Other suitable radicals are described in the above-mentioned patent applications.

Z2: A -$CONR^9R^{10}$ or $COOR^{11}$ radical, wherein R^{11} is an alkyl group containing from 1 to 8 carbon atoms, an aromatic group or an alkylaromatic group, such as, e.g., benzyl; the aromatic group preferably contains 6 or 10 carbon atoms and the alkylaromatic group preferably contains from 7 to 11 carbon atoms; the aromatic group may be substituted with alkyl groups (preferably containing from I to 3 carbon atoms)or polyethoxy groups (preferably containing from 1 to 6 ethoxy units).

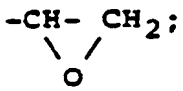
R^9 and R^{10}, eiher equal to, or different from, each other, have the same meaning as R^{11};

or a radical:



wherein Ar is an aromatic group preferably containing 6 or 10 carbon atoms;

or and -OH; -NCO;



-NHR^{11}; -COR^{11}; -$SiR^{12}_t(OR^{13})_{3-t}$ radical,

wherein R^{12} and R^{13}, either equal to, or different from, each other, have the same meaning as R^{11} , and wherein t is zero, 1, or 2.

Z3: a radical containing a polymerizable unsaturation of ethylenic type;

Z4: a radical belonging to Z1 class, containing one or more R^{11} substituents, wherein R^{11} has the above

indicated meaning.

H) $AO-(C_2F_4O)_k(CF_2O)_l-A'$

wherein the C_2F_4O and CF_2O units are randomly distributed throughout the chain;

k and l are integers; the k/l ratio is comprised within the range of from 0.3 to 5;

$A' = -CFX-YZ_p$

A is A' or a perfluoroalkyl radical containing from 1 to 3 carbon atoms; p, X, Y and Z have the same meaning as above stated.

The average molecular weight is comprised within the range of from 1 000 to 20 000.

J) $AO-(C_3F_6O)_f(C_2F_4O)_g(CFXO)_h-A'$

wherein the C_3F_6O, C_2F_4O and CFXO units are randomly distributed throughout the chain;

f, g and h are integers; the f/(g + h) ratio is comprised within the range of from 1 to 50;

the g/h ratio is comprised within the range of from 1 to 10;

A, A' and X have the same meaning as above stated;

the average molecular weight is comprised within the range of from 500 to 20 000.

K)

$$AO-\left(\begin{array}{c} R^{14} \\ | \\ C-CF_2-CF_2-O \\ | \\ R^{15} \end{array}\right)_m-A'$$

wherein R^{14} and R^{15}, either equal to, or different from, each other, are selected from H, Cl and F; a fluorine atom in $-CF_2-$ moieties may be substituted by H, Cl, a perfluoroalkoxy group (preferably containing from 1 to 12 carbon atoms) or a perfluoroalkyl group (preferably containing from 1 to 4 carbon atoms).

When the compound contains

$$\left(\begin{array}{c} R^{14} \\ | \\ -C-CF_2-CF_2-O- \\ | \\ R^{15} \end{array}\right)$$

units which are different from each other these units are randomly distributed throughout the chain; m is an integer chosen so that the average molecular weight is comprised within the range of from 1 500 to 8 000.

The end groups belonging to Z3 class are selected, in particular, from methacryl, acryl, cinnamic, vinyl, allyl, vinylether and allylether radicals.

The organic bridging radical Y can be, for example:

$-CH_2O-$, $-CH_2-O-CH_2-$, $-CH_2(OCH_2CH_2)_n-$ (wherein n is an integer comprised within the range of from 1 to 3), $-CF_2-$, $-CF_2O-$, $-CH_2-$, $-CONR^{11}-$, -COO-, -COS-, -CO-, $-CH_2NR^{11}-$, $-CH_2S-$, wherein R^{11} has the above specified meaning.

Other suitable bridging radicals Y are disclosed, as X or Y radicals, in U S-A-4094911.

The bi-functionalized perfluoropolyethers belonging to (F), (H), (J) and (K) classes can also be used, as explained in EP-A-215492 in the form of their products of polycondensation with other polycondensible monomers, i.e., e.g., as polyurethanes, polyureas, polyesters, polyamides, polyethers, polyimides and polyamic acids.

The monofunctional or bifunctional perfluoropolyethers belonging to (G), (H), (J) and (K) classes, containing Z3 end groups, i.e., those containing a polymerizable unsaturation of ethylenic type, can be also used in the form of their polymerization products, as disclosed in EP-A-215492.

The polytetrafluoroethylene, or its copolymer to be used in the present invention, can be obtained by means of known methods. It can be directly synthetized with the desired molecular weight, as described, e.g., by Mc Cane in "Encyclopaedia of Polymer Science and Technology", vol. 13, page 623, Interscience, New York, 1970.

As an alternative, by starting from an emulsion polymer or copolymer, having too high an average molecular weight, such molecular weight can be reduced by means of gamma radiation, as described, e.g., in Journal of Applied Polymer Science, Vol. 26, page 1373, 1981.

The amount of polytetrafluoroethylene or of its copolymer in the mixture of protective agents according

to the present invention is generally comprised within the range of from 2 to 30% by weight relative to the mixture, the mixture preferably containing from 10 to 20% thereof.

In the two-component mixture, in addition to polytetrafluoroethylene or its copolymer, a neutral perfluoropolyether or a functionalized perfluoropolyether or fluoropolyether is used. In the three-component mixtures, both said polyether types are present; in said three-component mixtures, the weight ratio of the functionalized perfluoropolyether or fluoropolyether to the neutral perfluoropolyether is equal to, or higher than, 0.01; said ratio is preferably comprised within the range of from 0.1 to 0.6.

The either neutral or functionalized polyether, or their mixture, can be used as such, or dissolved in a chlorofluorocarbon or in a fluorocarbon. Particularly suitable is 1,1,2-trichloro-1,2,2-trifluoro-ethane. In this latter case, the solution usually contains from 30 to 90% by weight of polyether.

Since polytetrafluoroethylene or its copolymer, are neither soluble in either functionalized or non-functionalized perfluoropolyethers or fluoropolyethers, nor in said solvents, they are introduced into the mixture in the solid state. More precisely, by suitably stirring, a suspension is prepared of the polymer or copolymer in the liquid phase constituted by the polyether(s) and the possible solvent, and the suspension is applied to the materials or structures to be protected.

The application of the suspension of protective agents on the materials or structures is carried out by suitable means: for example, it can be carried out by spraying an atomized - with or without compressed air - liquid stream, or by spreading by brush.

The amount of protective mixture to be applied to the surfaces to be protected may vary within wide limits, as a function of the nature of the material to be treated, in particular, of its porosity. Obviously, for porous materials, larger amounts are used. Usually, amounts comprised within the range of from 10 g to 500 g/m^2 of surface to be treated are used.

Except for those cases in which products are used, which derive from the polycondensation or ethylenic polymerization of functionalized perfluoropolyethers or fluoropolyethers, the protective composition can be removed from the materials and structures to which it has been applied, by treating such materials and structures first with 1,1,2-trichloro-1,2,2-trifluoroethane in order to remove most composition, and then with compressed air, in order to remove the residues of polytetrafluoroethylene or of its copolymer.

The present invention also relates to a process for preventing or eliminating the effects of decay caused on materials for the building industry and for linings, by the use of inks, spray paints or brush paints, coloured chalks, posted-up placards and the like.

The Applicant found that by using either a perfluoropolyether, or a fluoropolyether having at least one end group consisting of a functional group capable of forming a chemical and/or physical bond with the material to be protected, either alone, or optionally, in mixture with either one or both products selected from the following classes:

(1) polytetrafluoroethylene, or a tetrafluoroethylene copolymer containing up to 12 mol % of other perfluorinated monomers, with said homopolymer or copolymer being used in the form of a fine powder, present in an amount comprised within the range of from 2 to 30% by weight;

(2) a perfluoropolyether containing perfluoroalkyl end-groups; surfaces of materials having a porosity even higher than 10%, and preferably lower than 30% can be protected over a very long period of time.

As tetrafluoroethylene copolymers suitable for use, there can be used, e.g. those indicated above.

The average molecular weight of the homopolymer or copolymer of tetrafluoroethylene, the average size of the primary particles of homopolymer or copolymer, the average molecular weight of the perfluoropolyether not bearing functional groups, and the average molecular weight of the functionalized perfluoropolyether or fluoropolyether are as indicated above.

The perfluoropolyethers not bearing functional groups and the functionalzed perfluoropolyethers may contain oxaperfluoroalkylene units belonging to types (I) to (IX) as described above.

The functionalized fluoropolyethers may contain the units (X) and (XI) as described above.

Specific examples of functionalized perfluoropolyethers and specific examples of the neutral perfluoropolyethers, i.e. perfluoropolyethers containing perfluoroalkyl end groups, are those belonging to the classes described above.

The polytetrafluoroethylene, or the tetrafluoroethylene copolymer to be used in the present invention can be obtained by the methods indicated above.

The amount of polytetrafluoroethylene, or of tetrafluoroethylene copolymers in mixture with protecting agents according to the present invention is generally comprised within the range of from 2 to 30% by weight relative to the total mixture.

Preferably, the mixture comprises from 10 to 20% thereof.

The functionalized polyether, either alone, or optionally in admixture with polyethers bearing functional groups, can be used as such, or it can be dissolved in a chlorofluorocarbon or fluorocarbon as indicated

above.

In those mixtures which contain polytetrafluoroethylene or tetrafluoroethylene copolymers, the weight ratio of the functionalized perfluoropolyether or functionalized fluoropolyethers to neutral perfluoropolyethers is equal to or larger than 0.01; such a ratio is preferably comprised within the range of from 0.1 to 0.6.

Since polytetrafluoroethylene and tetrafluoroethylene copolymers are neither soluble in perfluoropolyethers or fluoropolyethers whether functionalized or not, nor in the above said solvents, they are incorporated into the mixture in the solid state as indicated above.

Application of the protective agents suspension to materials or buildings is carried out by using the means indicated above.

The amount of protecting agent to be applied to the surfaces to be protected is as indicated above.

Except for those cases in which products of polycondensation or ethylenic polymerization of functionalized perfluoropolyethers or fluoropolyethers are used, the protecting composition can be removed from the materials and buildings to which it was applied as indicated above.

The following examples are given for merely illustrative purposes, and are not limitative of the present invention.

EXAMPLE 1

Nine marble test pieces having a porosity of 1.7% are used. The test pieces have a size of 50 x 50 x 20 mm.

Test piece 1 is not treated. Different protective compositions are applied by means of a brush to the other test pieces.

To test pieces 2-5, variable amounts of neutral perfluoropolyether Fomblin® YR and of polytetrafluoroethylene are applied. (To test piece 5 no polytetrafluoroethylene is applied).

The neutral perfluoropolyether Fomblin®YR manufactured by Montefluos S.p.A. has the formula:

$$R_f\text{-}O\text{-}(C_3F_6O)_a(\underset{\displaystyle CF_3}{\underset{|}{CF}}\text{-}O)_b(CF_2O)_c\text{-}R'_f$$

wherein: R_f is CF_3 and R'_f is CF_3.

Its average molecular weight is of approximately 6 500.

To test pieces 6-9, variable amounts of a mixture of a neutral perfluoropolyether Fomblin® YR and of an amide functionalized perfluoropolyether are applied together with variable amounts of polytetrafluoroethylene (to test piece 9, no polytetrafluoroethylene is applied).

The ratio by weight of neutral perfluoropolyether to the amidic perfluoropolyether is of 60:40.

The amidic perfluoropolyether has the formula:

$$R_f\text{-}O\text{-}(C_3F_6O)_a(\underset{\displaystyle CF_3}{\underset{|}{CFO}})_b(CF_2O)_c\text{-}CF_2\text{-}CONH\text{-}iso\text{-}C_4H_9$$

wherein: R_f is CF_3. Its average molecular weight is of approximately 5.000.

Polytetrafluoroethylene is Algoflon® L206 , manufactured by Montefluos S.p.A.. The size of the primary particles of polytetrafluoroethylene is comprised within the range of from 0.15 to 0.25 μm.

The amount of protective composition applied by brush-spreading to test pieces 2-9 is expressed as grams per square metre of surface area, and is reported in Table 1A.

The efficacy of the treatment is evaluated on the basis of the amount of water absorbed by the various test pieces within 60 minutes and is expressed by the percent ratio:

$$\frac{\text{(water absorbed by untreated test piece) less (water absorbed after treatment)}}{\text{(water absorbed by untreated test piece)}}$$

The test is carried out by applying to a face of the test pieces a device constituted by a glass cylinder filled with water, and connected with a graduated micropipette, which allows the amount of water absorbed by the surface of contact with the sample to be measured. Such equipment is described in the document published by Unesco-Rilem PEM Group with No. 78,182. The reading of the absorbed water is carried out at prefixed time intervals, and the quantity read is expressed as g/cm^2 of surface area.

The amount of water absorbed by the various test pieces (expressed as g/cm^2 and the corresponding efficacy of the treatment are reported in Table 1A.

It can be observed that the use of the compositions according to the present invention yields better results than the use of either the neutral or functionalized perfluoropolyether alone, although a smaller amount of protective agents is used.

On some test pieces, also the permability to water vapour was determined. The permeability of the protective coatings to water vapour is a necessary feature, in that it enables any water which may be present under the coating to evaporate.

The measurement of water vapour permeability is carried out as follows: the test piece is fastened, by means of a sealing agent, to a plexiglas vessel, according to the arrangement as disclosed in EP-A-192493.

Inside the vessel, 2.5 cm^3 of water are previously introduced; the whole assembly is weighed and is then introduced inside a calcium-chloride desiccator.

At pre-established time intervals, the assembly constituted by the test piece and the vessel is weighed. The tests are run at the controlled constant temperature of 20 °C. The test is discontinued after 144 hours, and the end weight losses are compared to those of the untreated sample, to which a permeability of 100% is attributed.

The test results are reported in Table B.

It can be observed that the protective compositions according to the present invention supply a permeability to water vapour slightly lower than that obtained with perfluoropolyether alone. Anyway, such a permeability remains very good, in that the permeability values are regarded as good from 50% up.

TABLE 1A

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount $g/cm^2 \times 10^{-4}$	Treatment Efficacy %
1	Marble	None	-	from 47.40 to 74.72 according to test	-
2	"	Fomblin YR 95% + PTFE 5%	45	3.80	92
3	"	Fomblin YR 90% + PTFE 10%	56	2.92	95
4	"	Fomblin YR 85% + PTFE 15%	55	2.96	95

TABLE 1A (continued)

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount g/cm^{2}x10^{-4}	Treatment Efficacy %
5	Marble	Fomblin® YR 100%	81	21.20	71
6	"	Amidic mixture 95% + PTFE 5%	35	2.00	96
7	"	Amidic mixture 90% + PTFE 10%	33	2.56	95
8	"	Amidic mixture 85% + PTFE 15%	37	2.36	96
9	"	Amidic mixture 100%	59	16.96	84

TABLE 1B

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Permeability to water
1	Marble	None	-	100%

TABLE 1B (continued)

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Permeability to water
5	Marble	Fomblin® YR 100%	81	85%
2	"	Fomblin® YR 95% + PTFE 5%	45	80%
3	"	Fomblin® YR 90% + PTFE 10%	56	80%
4	"	Fomblin® YR 85% + PTFE 15%	55	70%

Example 2

The tests are carried out on a sandstone having a porosity of 8.5%.The modalities are the same as of Example 1, except for the fact that the test of water absorption is carried out in 30 minutes, and the permeability to water vapour is not determined.

The experimental data and the results are reported in Table 2.

Example 3

The tests of Example 2 are carried out on a Vicenza stone having a porosity of 30%.

The experimental data and the results are reported in Table 3.

It is observed that the mixtures of protective agents according to the present invention give a high treatment efficacy also in case of very porous materials.

TABLE 2

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount g/cm^{2}x10^{-4}	Treatment Efficacy %
11	Sand-stone	None	-	from 211.48 to 250.64 accord-ing to test	-
12	"	Fomblin® YR 95% + PTFE 5%	101	21.44	90
13	"	Fomblin® YR 90% + PTFE 10%	127	22.44	91
14	"	Fomblin® YR 85% + PTFE 15%	119	8.36	96
15	"	Fomblin® YR 100%	188	49.24	77

TABLE 2 (continued)

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount g/cm^{2}x10^{-4}	Treatment Efficacy %
16	Sand-stone	Amidic mix-ture 95% + PTFE 5%	74	8.20	96
17	"	Amidic mix-ture 90% + PTFE 10%	80	8.80	96
18	"	Amidic mix-ture 85% + PTFE 15%	79	5.40	98
19	"	Amidic mix-ture 100%	115	33.36	84

TABLE 3

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount g/cm^{2}x10^{-4}	Treatment Efficacy %
21	Vicenza Stone	None	-	from 2,015.48 to 2,212.48 according to test	-

TABLE 3 (Continued)

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount $g/cm^2 \times 10^{-4}$	Treatment Efficacy %
22	Vicenza Stone	Fomblin® YR 95% + PTFE 5%	365	116.52	95
23	"	Fomblin® YR 90% + PTFE 10%	308	54.92	97
24	"	Fomblin® YR 85% + PTFE 15%	209	35.88	98
25	"	Fomblin® YR 100%	2,120	769.60	62
26	"	Amidic mixture 95% + PTFE 5%	173	57.36	97
27	"	Amidic mixture 90% + PTFE 10%	177	36.76	98
28	"	Amidic mixture 85% + PTFE 15%	181	34.04	98

TABLE 3 (Continued)

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount $g/cm^2 x 10^{-4}$	Treatment Efficacy %
29	Vicenza Stone	Amidic mixture 100%	2,354	608.00	69

Example 4

The tests of Example 2 are repeated on a Lecce stone having a porosity of 42%.
The experimental data and the results are reported in Table 4.

Example 5

The tests were carried out on a concrete having 18% of porosity. The material was prepared by starting from: Portland 425 cement, using a water/cement ratio of 0.425 and a cement/inerts (sand and gravel) ratio of 0.3.

The protective agent is constituted by a mixture of a neutral perfluoropolyether, a carboxy-functionalized perfluoropolyether and polytetrafluoroethylene.

The neutral pefluoropolyether is the same Fomblin®YR as of Example 1.

The functionalized perfluoropolyether has the formula:

$$R_f\text{-}O\text{-}(C_3F_6O)_a(\underset{\displaystyle CF_3}{\overset{\displaystyle |}{CFO}})_b(CF_2\text{-}O)_c\text{-}CF_2\text{-}COOH$$

wherein R_f is $-CF_3$, and has an average molecular weight of approximately 2 000.

The ratio of the functionalized perfluoropolyether relatively to the neutral perfluoropolyether is of 20:80 parts by weight.

Mixtures are used, which contain various amounts of Algoflon L206 polytetrafluoroethylene.

The procedure of Example 2 is followed.

The experimental data and the results obtained are reported in Table 5.

TABLE 4

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount $g/cm^2 \times 10^{-4}$	Treatment Efficacy %
31	Lecce Stone	None	-	from 2 146.80 to 2 514 20 according to test	-
32	"	Fomblin® YR 95% + PTFE 5%	199	233.72	91
33	"	Fomblin® YR 90% + PTFE 10%	185	60.80	98

TABLE 4 (Continued)

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount $g/cm^2 x 10^{-4}$	Treatment Efficacy %
34	Lecce Stone	Fomblin® YR 85% + PTFE 15%	194	23.36	99
35	"	Fomblin® YR 100%	2,316	989.00	55
36	"	Amidic mixture 95% + PTFE 5%	174	54.04	98
37	"	Amidic mixture 90% + PTFE 10%	162	8.16	100
38	"	Amidic mixture 85% + PTFE 15%	152	2.52	100
39	"	Amidic mixture 100%	1,861	428.20	81

TABLE 5

Test No.	Treated Material	Protective Agents (% by weight)	Amount of Applied Protective Agents g/m^2	Absorbed Water Amount g/cm^{2}x10^{-4}	Treatment Efficacy %
41	Concrete	None	-	from 3,860.80 to 5,130.40 according to test	-
42	"	Carboxylic mixture 95% + PTFE 5%	150	1,261.00	70
43	"	Carboxylic mixture 90% + PTFE 10%	150	650.04	85
44	"	Carboxylic mixture 85% + PTFE 15%	150	442.08	90
45	"	Carboxylic mixture 100%	150	2,130.40	50

Example 6

A slab of Carrara marble was used, whose surface had a porosity of 0.3%. Such a slab had a thickness of 4 cm, with sides of 120x180 cm, and was subdivided into two portions with the same surface area; to one of said portions, an amount of FOMBLIN®Y MET (a perfluoropolyether with perfluoroalkyl end groups by Montefluos S.p.A.) of 80 g/m^2 was applied.

The application was carried out by means of a brush, after a cleaning of the surface, in order to remove any dust or foreign substances, by means of two successive operations, spaced out by approximately 70 hours.

Five days after the last application, the slab surface treated with the protecting agent was slightly darker

and more glossy than the original surface was before the treatment.

Now, the following operations were carried out:

a) "writing" tests, carried out by starting from the untreated surface portion, and proceeding towards the protected surface, by using:

1. Spraying of a quick-drying red nitrocellulose lacquer (a commercial can);
2. Spraying of a normal red lacquer (a commercial can);
3. Brush-painting with a red nitrocellulose lacquer;
4. White chalk of blackboard type.

On the untreated surface, in all cases the performed writing action resulted evident, whilst on the protected surface portion, the following was respectively observed:

1. A uniform, poorly perceivable trace, constituted by lacquer droplets, trending to coagulate;
2. As above, with the presence of coagulums and immediate formation of large paint drops flowing downwards;
3. The brush "slips", leaving an imperceptible trail of colour;
4. Chalk "slips" without leaving any colour.

b) Cleaning test. Approximately 30 hours after the test disclosed under (a), tests on the "written" surface were carried out. The test was carried out with dry cotton cloths, soaked with acetone and replaced by other clean cloths, as they became saturated with paint and solvent.

In the case of the protected surface, the retained paint was fully and quickly removed, and the normal appearance of marble was restored. In case of the untreated surface, the cleaning, besides being more toilsome, did not allow satisfactory results to be reached, owing to the persisting of evident colour areas, caused by the marble absorbing the paint-solvent solution.

The same cleaning results are also obtained when trichloroethylene is used as the solvent.

(Comparative) Example 7

The test is carried out in the same way as disclosed in Example 1, but the cleaning step (the (b) step) is carried out 90 days later. The cleaning of the parts treated with the protective agent does not yield satisfactory results, due to the persistence of colour areas.

Example 8

A set of plates of Carrara marble with porosity of 1.5% were used, with each one of them being subdivided into two portions of equal surface area; to each of said portions, variable amounts of perfluoroalkyl-terminated perfluoropolyethers of Fomblin® Y type, of perfluoropolyethers with isobutyl ester (IBE) end groups, and of perfluoropolyethers with isobutyl-amide end groups (IBA) were applied.

The IBE-terminated perfluoropolyethers correspond to the general formula (E) wherein R_f = CF_3 and D = $CF_2COOC_4H_9$ (ISO), whilst the IBA-terminated perfluoropolyethers correspond to the general formula (E) wherein R_f = CF_3 and D = $CF_2CONH(C_4H_9)$ (ISO).

The application was carried out as reported in Example 6.

Ninety days after the treatment, the following operations were carried out on the dry surfaces:

a) "writing" tests, carried out by starting from the untreated surface portion, and proceeding towards the protected surface portion, by using:

1. Spraying of a quick-drying red nitrocellulose lacquer (a commercial can);
2. Spraying of a normal red lacquer (a commercial can);
3. Brush-painting with a red nitrocellulose lacquer;
4. White chalk of blackboard type.

On the untreated surface, in all cases the performed writing action resulted evident, whilst on the protected surface portion, the following was respectively observed:

1. A uniform, poorly perceivable trace, constituted by lacquer microdroplets, tending to coagulate;
2. As above, with the presence of coagulums and immediate formation of large paint drops flowing downwards;
3. The brush "slips", leaving an imperceptible trail of colour;

4. Chalk "slips" without leaving any colour.

b) Cleaning test. Approximately 72 hours later than the test disclosed under (a), tests on the "written" surface were carried out. The test was carried out with dry cotton cloths, soaked with acetone, and replaced by other clean cloths, as they became saturated with paint and solvent.

In case of protected surface, the retained paint was fully and quickly removed, and the normal appearance of marble was restored. In case of untreated surface, the cleaning, besides being more toilsome, does not allow satisfactory results to be reached, due to the persistence of evident colour areas, caused by the the marble absorbing the paint-solvent solution.

The following is a synoptic table of the results:

Plate No.	1	2	3	4
Product and g/m^2	Untreated	Y MET 80 g/m^2	IBE 50 g/m^2	IBA 50 g/m^2
Results after Cleaning	Evident traces	Slight halo	Complete disappear-ance	Complete disappear-ance

Example 9

A set of small plates of Vicenza Stone (an organogen limestone) was used, which had a porosity of 30%, subdivided into two portions having the same surface area, to each of which variable amounts were applied of perfluoroalkyl-terminated perfluoro-polyethers of FOMBLIN(R) Y MET type, and of IBE-terminated and IBA-terminated perfluoropolyethers as defined in Example 8, as well as of a mixture containing 85% by weight of isobutylamino-terminated perfluoropolyethers and 15% of fine PTFE powder, and finally of perfluoropolyethers (AI) having the general formula of hereinabove reported (E) type, wherein R_f = CF_3 and D = CF_2COOH. Ninety days after the treatment, the following operations were carried out on the dry surface:

(a) writing tests; and

(b) cleaning tests, according to the same modalities as set out in the previous Examples.

In particular, the cleaning tests were carried out 72 hours after the writing test.

The results obtained were the following:

Plate

No.	1	2	3	4	5	6
Product and g/m^2	Untreated	Y MET 600 g/m^2	IBE 300 g/m^2	IBA 400 g/m^2	IBA+PTFE 200 g/m^2	Al 150 g/m^2
Results after Cleaning	Paint persist-ence	Toned down image	Light halo	Light halo	Complete disappear-ance	Complete disappear-ance

Claims

1. A process for the protection of stone materials, marble, bricks and concrete, and of structures obtained from such materials, against the decay caused by atmospheric agents and pollutants, by means of application of a protective agent to the surface of said materials and structures, characterized in that the protective agent comprises a mixture of:

1) polytetrafluoroethylene, or a tetrafluoroethylene copolymer containing up to 12 mol % of other perfluorinated monomers, with said homopolymer or copolymer being used as a fine powder;

2) a perfluoropolyether not bearing functional groups; and/or

3) a perfluoropolyether or a fluoropolyether having a chain end, or both chain ends, constituted by a functional group capable of forming a chemical and/or physical bond with the material to be protected, or a product of polycondensation or ethylenic polymerization of the above-said functionalized perfluoropolyether or fluoropolyether.

2. The process according to claim 1, characterized in that the average size of the primary particles of tetrafluoroethylene homopolymer or copolymer is comprised within the range of from 0.05 to 0.5 μm.

3. The process according to claim 1 or 2, characterized in that the average molecular weight of tetrafluoro ethylene homopolymer or copolymer is comprised within the range of from 100 000 to 2 000 000.

4. The process according to one or more of the preceding claims, characterized in that the average molecular weight of the perfluoropolyether not bearing functional groups is comprised within the range of from 3 000 to 16 000.

5. The process according to one or more of the preceding claims, characterized in that the perfluoropolyether or fluoropolyether having a chain end, or both chain ends, constituted by a functional group, has an average molecular weight comprised within the range of from 500 to 20 000.

6. The process according to one or more of the preceding claims, characterized in that the perfluoropolyether not bearing functional groups, or the perfluoropolyether having a chain end, or both chain ends, constituted by a functional group, contain repeating oxyperfluoroalkylene units selected from:

I) $(CF_2\text{-}CF_2O)$ and (CF_2O), with such units being randomly distributed along the perfluoropolyether chain;

II) $(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{CF}}O)$ and $(CFXO)$,

wherein X is either F or CF_3, with said units being randomly distributed along the chain:

III) $(CF_2\text{-}CF_2O)$, $(CF_2\text{-}\underset{\displaystyle CF_3}{\underset{|}{CF}}O)$ and $(CFXO)$,

wherein X is either F or CF_3, with such units being randomly distributed along the chain;

IV) $(\underset{\displaystyle CF_3}{\underset{|}{CF}}\text{-}CF_2O)$;

V) $(CF_2\text{-}CF_2\text{-}CF_2\text{-}O)$;

VI) $(CF_2-\underset{\underset{CF_3}{|}}{CFO})_{a'}-CF_2-(R''_f)_n-CF_2O(-\underset{\underset{CF_3}{|}}{CF}-CF_2-O)_{b'}$,

wherein R''_f is a fluoroalkylene group; n is either 0 or 1; a' and b' are integers, and the (a' + b') sum is equal to or higher than 2;

VII) (CF_2-CF_2O);

VIII) $$\left(\underset{\underset{CF_3}{|}}{C}-O-\underset{\underset{R''_fR''_f}{|}}{C}-\underset{\underset{R''_fR''_f}{|}}{C}-O\right)$$

wherein the R''_f groups, either equal to or different from each other, represent a fluorine atom or a perfluoroalkyl group;

IX) $(CF_2-CF_2-CF_2O)$.

7. The process according to one or more of the preceding claims, characterized in that the fluoropolyether having one chain end, or both chain ends constituted by a functional group, has units selected from:

X) $(CF_2-CF_2-CF_2O)$; and

XI) $(CF_2-CF_2-CH_2-O)_{p'}-R^{iv}_f-O-(CH_2-CF_2-CF_2O)_{q'}$,

wherein R^{iv}_f is a fluoroalkylene group and p' and q' are zero, or integers, and the (p' + q') sum is equal to or larger than 2.

8. The process according to one or more of the preceding claims, characterized in that the perfluoropolyether not bearing functional groups is selected from one of the following classes:

A) $$R_f-O-(C_3F_6O)_a(\underset{\underset{CF_3}{|}}{CF}-O)_b(CF_2O)_c-R'_f$$

wherein: R_f and R'_f, either equal to or different from each other, are selected from CF_3, C_2F_5 and C_3F_7; the C_3F_6O (oxytrifluoromethyltrifluoroethylene),

$$\underset{\underset{CF_3}{|}}{CF-O}$$

and CF_2O units are randomly distributed along the chain;
a is an integer;
b and c are integers or zero;
when the (b + c) sum is different from zero, the a/(b + c) is comprised within the range of from 5 to 40;
the average molecular weight is comprised within the range of from 4 000 to 10 000.

B) $CF_3O-(C_2F_4O)_d(CF_2O)_e-CF_3$
wherein the C_2F_4O and CF_2O units are randomly distributed along the chain;
d and e are integers;
the d/e ratio is comprised within the range of from 0.3 to 5;
the average molecular weight is comprised within the range of from 3 000 to 16 000.

C) $CF_3O-(C_3F_5O)_f(C_2F_4O)_g(CFXO)_h-CF_3$
wherein the C_3F_6O, C_2F_4O and CFXO units are randomly distributed along the chain;
f, g and h are integers;
the f/(g + h) ratio is comprised within the range of from 1 to 50;
the g/h ratio is comprised within the range of from 1 to 10.

X is F or CF_3;
the average molecular weight is comprised within the range of from 4 000 to 12 000.
D) $R^3_fO-(CF_2-CF_2-CF_2O)_jR^4_f$
wherein R^3_f and R^4_f, either equal to, or different from each other, are $-CF_3$ or $-C_2F_5$ and
j is an integer having such a value, that the average molecular weight is comprised within the range of from 4 000 to 16 000.

9. The process according to one or more of the preceding claims, characterized in that the perfluoropolyether having one chain end, or both chain ends constituted by a functional group capable of forming a chemical and/or physical bond with the material to be protected is selected from one of the following classes:

$$E)\quad R_f-O-(C_3F_6O)_a(\underset{\displaystyle CF_3}{\overset{\displaystyle |}{CF-O}})_b(CF_2O)_c-D$$

wherein:
R_f is perfluoroalkyl group containing from 1 to 3 carbon atoms; the C_3F_6O,

$$\overset{\displaystyle |}{\underset{\displaystyle CF_3}{CF-O}}$$

and CF_2O units are randomly distributed along the chain;
a is an integer;
b and c are integers or zero;
when the (b + c) sum is different from zero, the a/(b + c) ratio is comprised within the range of from 5 to 40;
D is a $-CFX-COZ'$ group, wherein X = F or CF_3 and Z' = OH, OR^5 or NR^6R^7, wherein R^5 is an alkyl group containing from 1 to 8 carbon atoms, an aromatic group or an alkylaromatic group, wherein the aromatic group may be substituted with alkyl groups or polyethoxy groups; the average molecular weight is comprised within the range of from 500 to 10,000.
F) $D'-(C_2F_4O)_d(CF_2O)_e-D'$
wherein the C_2F_4O and CF_2O units are randomly distributed along the chain;
d and e are integers; the d/e ratio is comprised within the range of from 0.3 to 5;
D' = CF_2-COZ', wherein Z' has the above disclosed meaning;
the average molecular weight is comprised within the range of from 1 000 to 20 000.

$$G)\quad R_f-O-(C_3F_6O)_a(\underset{\displaystyle CF_3}{\overset{\displaystyle |}{CF-O}})_b(CF_2O)_c-CFX-YZ_p$$

wherein:
R_f is a perfluoroalkyl group containing from 1 to 3 carbon atoms; the C_3F_6O,

$$\overset{\displaystyle |}{\underset{\displaystyle CF_3}{CF-O}}$$

and CF_2O units are randomly distributed along the chain;
a is an integer;
b and c are integers or zero;
when the (b + c) sum is different from zero, the a/(b + c) ratio is comprised within the range of from 5 to 40.
p can be 1 or 2;
Y is an either bivalent or trivalent bridging organic radical; the average molecular weight is comprised within

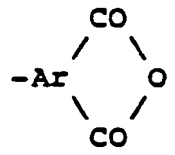
the range of from 500 to 10 000.

Z is a functional radical capable of forming a chemical and/or physical bond with the material to be protected, and is selected from the group consisting of Z1, Z2, Z3, Z4, wherein:

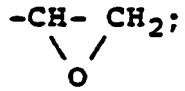
Z1: a non-aromatic, non-fluorinated organic radical not containing active hydrogen atoms, containing two or more heteroatoms, either equal to, or different from each other and selected from O, N, S, Se and P, which are donors of electronic doublets and are situated in 1-3, 1-4 or 1-5 position relative to each other, or an aromatic radical optionally containing heteroatoms, selected from those indicated above, capable of forming coordination or charge-transfer bonds.

Z2: A $-CONR^9R^{10}$ or $COOR^{11}$ radical, wherein R^{11} is an alkyl group containing from 1 to 8 carbon atoms, an aromatic group or an alkylaromatic group, wherein the aromatic group may be substituted with alkyl groups or polyethoxy groups.

R^9 and R^{10}, either equal to, or different from, each other, have the same meaning as R^{11}; or a radical:



wherein Ar is an aromatic group; or an -OH; -NCO;



$-NHR^{11}$; $-COR^{11}$; $-SiR^{12}_t(OR^{13})_{3-t}$ radical, wherein R^{12} and R^{13}, either equal to, or different from, each other, have the same meaning as R^{11}, and wherein t is zero, 1, or 2.

Z3: a radical containing a polymerizable unsaturation of ethylenic type;

Z4: a radical belonging to Z1 class, containing one or more R^{11} substituents, wherein R^{11} has the same meaning as above indicated.

H) $AO-(C_2F_4O)_k(CF_2O)_l-A'$

wherein the C_2F_4O and CF_2O units are randomly distributed along the chain;

k and l are integers; the k/l ratio is comprised within the range of from 0.3 to 5;

$A' = -CFX-YZ_p$

A is A' or a perfluoroalkyl radical containing from 1 to 3 carbon atoms; p, X, Y and Z have the same meaning as above stated;

the average molecular weight is comprised within the range of from 1,000 to 20,000.

J) $AO-(C_3F_6O)_f(C_2F_4O)_g(CFXO)_h-A'$

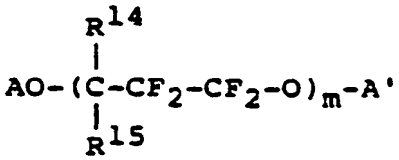
wherein the C_3F_6O, C_2F_4O and CFXO units are randomly distributed along the chain;

f, g and h are integers; the f/(g + h) ratio is comprised within the range of from 1 to 50;

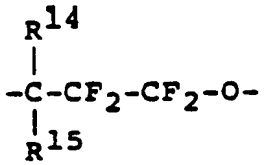
the g/h ratio is comprised within the range of from 1 to 10;

A, A' and X have the same meaning as above stated, the average molecular weight is comprised within the range of from 500 to 20,000.

K)



wherein R^{14} and R^{15}, either equal to, or different from, each other, are selected from H, Cl and F; a fluorine atom in $-CF_2-$ moieties may be substituted by H, Cl, a perfluoroalkoxy group or a perfluoroalkyl group when the compound contains



units which are different from one another, these units are randomly distributed along the chain, m is an integer chosen so that the average molecular weight is comprised within the range of from 1 500 to 8 000.

10. The process according to one or more of the preceding claims, characterized in that the Z3 radical is selected from methacryl, acryl, cinnamic, vinyl, allyl, vinylether and allylether radicals.

11. The process according to one or more of the preceding claims, characterized in that the organic bridging radical Y is selected from:
$-CH_2O-$, $-CH_2-O-CH_2-$, $-CH_2(OCH_2CH_2)n-$ (wherein n is an integer comprised within the range of from 1 to 3), $-CF_2-$, $-CF_2O-$, $-CH_2-$, $-CONR^{11}-$, $-COO-$, $-COS-$, $-CO-$, $-CH_2NR^{11}-$, $-CH_2S-$, wherein R^{11} is an alkyl group containing from 1 to 8 carbon atoms, an aromatic group or an alkylaromatic group, wherein the aromatic group may be substituted with alkyl groups or polyethoxy groups.

12. The process according to one or more of the preceding claims, characterized in that the mixture of protective agents contains from 2 to 30% by weight of tetrafluoroethylene homopolymer or copolymer.

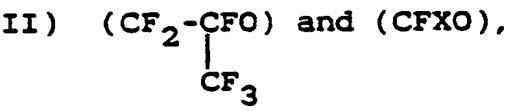
13. The process according to claim 12, characterized in that the mixture of protective agents contains from 10 to 20% by weight of tetrafluoroethylene homopolymer or copolymer.

14. The process according to one or more of the preceding claims, characterized in that the perfluoropolyether not bearing functional groups and/or the perfluoropolyether or the fluoropolyether having a chain end, or both chain ends, constituted by a functional group, are used in the form of a solution thereof in a chlorofluorocarbon or in a fluorocarbon.

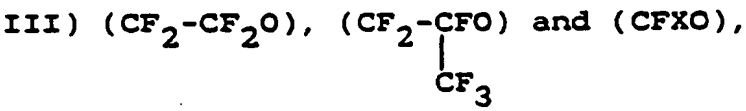
15. The process according to claim 14, characterized in that the chlorofluorocarbon is 1,1,2-trichloro-1,2,2-trifluoroethane.

16. The process according to one or more of the preceding claims, characterized in that the amount of protective agents applied to the materials or structures to be protected is comprised within the range of from 10 to 500 g/m^2 of surface area to be treated.

17. A process for protecting materials for building industry and linings, from paints, inks and the like, which comprises applying to the surface of such materials having porosity values not higher than 40%, a coating comprising a perfluoropolyether or a fluoropolyether having one chain end or both chain ends constituted by a functional group capable of forming a chemical and/or physical bond with the material to be protected; wherein such perfluoropolyether contains oxaperfluoroalkylene units selected from the following classes:
(I) (CF_2-CF_2O) and (CF_2O), with such units being randomly distributed along the perfluoropolyether chain;



wherein X is either F or CF_3, with said units being randomly distributed along the perfluoropolyether chain;



wherein X is either F or CF_3, with such units being randomly distributed along the perfluoropolyether chain;

IV) $(CF(CF_3)-CF_2O)$;

V) $(CF_2-CF_2-CF_2O)$;

VI) $(CF_2-CF(CF_3)O)_{a'}-CF_2-(R''_f)_{n'}-CF_2O(-CF(CF_3)-CF_2-O)_{b'}$

wherein R''_f is a fluoroalkylene group;
n' is either 0 or 1;
a' and b' are integers, and the $(a' + b')$ sum is equal to or higher than 2;
VII) (CF_2-CF_2O);

VIII) $(C(CF_3)_2-O-C(R''_f)_2-C(R''_f)_2-O)$

wherein the R''_f groups, either equal to or different from each other, represent a fluorine atom or a perfluoroalkyl group; and
IX) $(CF_2O-CF_2-CF_2O)$;
and wherein the fluoropolyether contains the following units:
X) $(CH_2-CF_2-CF_2O)$; or
XI) $(CF_2-CF_2-CH_2O)_{p'}-R^{IV}_f-O-(CH_2CF_2-CF_2O)_{q'}$
wherein:
R^{IV}_f is a fluoroalkylene group and
p' and q' are zero, or integers, and the $(p' + q')$ sum is equal to or larger than 2.
such perfluoropolyether or fluoropolyether being used either alone or in mixture with a compound selected from one or both of the following classes:

(1) polytetrafluoroethylene or tetrafluoroethylene copolymer containing up to 12 mol % of other perfluorinated monomers, with said homopolymer or copolymer being used in a fine powder form;

(2) a perfluoropolyether having perfluoroalkyl end groups.

18. The process according to claim 17, wherein polytetrafluoroethylene or a tetrafluoroethylene copolymer is present in an amount of from 10 to 20% by weight.

19. The process according to claim 17 or 18 wherein the tetrafluoroethylene copolymer contains up to 10 mol % of hexafluoropropene, and up to 5 mol % of perfluoroalkylperfluorovinyl ether.

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(54) **Process for the protection of stone materials, marble, bricks and concrete from decay caused by atmospheric agents and pollutants or by mural writings with paints, inks and the like.**

(57) The present invention relates to a process for the protection of stone materials, marble, bricks and concrete, and of structures made from such materials, from the decay caused by atmospheric agents and pollutants or by mural writings with paints, inks and the like. The process comprises applying to the surface of said materials or structures a mixture which comprises:

1) polytetrafluoroethylene in the form of a fine powder;

2) a perfluoropolyether not bearing functional groups and/or

3) a perfluoropolyether or a fluoropolyether having one chain end, or both chain ends, constituted by functional groups which are capable of forming a chemical and/or physical bond with the material to be protected.

European Patent Office

EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 88112061.2

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
D,X	EP - A2 - 0 215 492 (AUSIMONT S.P.A.) * Totality * --	1,6-11,14,17	C 04 B 41/48
D,X	EP - A1 - 0 192 493 (AUSIMONT S.P.A. & CONSIGLIO NAZIONALE DELLE RICERCHE) * Claims * --	1,6-11,14,16,17	
Y	DE - A - 1 694 508 (E.I. DU PONT DE NEMOURS AND CO.) * Claims; page 9, lines 9-12 * ----	1,12,13,16	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 04 B
C 08 G
C 08 L
C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	12-05-1989	BECK

CATEGORY OF CITED DOCUMENTS :

X : particularly relevant if taken alone
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